OUTGASSING OF MATERIALS IN THE SPACE ENVIRONMENT

A THERMOKINETIC APPROACH

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ABSTRACT

Previous efforts to model the outgassing of polymers on space-craft have been partly empirical and partly educated guesses. None of these approaches have been successful in effectively describing the process in terms of time and temperature in such a manner that out-gassing could be predicted in advance so that valid assessments could be made of its effects on various optical systems.

This report provides a fresh approach to this problem by relating the outgassing to basic chemical reaction kinetics, which provides a powerful tool for such estimations and also provides an insight to the basic mechanisms involved. The general equations of the total outgassing quantity are derived, as well as the outgassing rates, as functions of time and temperature. The results are shown to be consistent with experimental data obtained in earlier programs. While there is much evidence that suggests outgassing is primarily a first-order reaction, the equations are presented here for both first-order and other-than-first-order reactions.

The power to the reaction-kinetics approach lies in its applicability whether the outgassing mechanism is due to desorption, diffusion, thermal decomposition or evaporation. It also illuminates those situations where only minor constituents of the parent material outgas, or where the entire substance may outgas.

To implement the use of this approach certain thermokinetic parameters must be measured for each material of interest. It is suggested that the necessary data can be obtained through sensitive thermogravimetric analysis (TGA) techniques.

1.0 INTRODUCTION

The outgassing of polymers in space can occur due to several mechanisms:

o Chain scission

o Desorption

o Improper catalyst/resin ratio or inadequate mixing or curing

o Evaporation

Chain scission occurs when a fragment of a molecular chain breaks off due to heat or radiation. While this process is normally associated with elevated temperatures, it will also occur at lower temperatures though at greatly reduced rates. Desorption occurs when absorbed gases or solvents become volatile in the vacuum of space. Frequently these may be noncondensable gases which are more correctly termed offgassing species. The occurrence of improper catalyst/resin ratio, which may be also due to nonuniform distribution of these components, leaves a residue of low molecular weight monomer or prepolymer and/or catalyst which because of its low molecular weight, is much more easily volatilized in the vacuum of space than the parent polymer. Also such materials can be expected to diffuse through the bulk material to the surface.

The processes of chain scission and of evaporation imply that the entire mass of the substance is ultimately available for outgassing. Where desorption or diffusion and vaporization of catalyst or monomer occurs, these processes involve only a small fraction of the parent material. These latter processes also have lower activation energies and therefore outgas much more readily than a decomposition process. The active mass of material available for outgassing (as contrasted with the total mass) will be seen to be a very important quantity as it enters into many of the equations and can influence the validity of the currently accepted NASA/ASTM Micro-VCM outgassing test. Also from a very practical standpoint it is probable that thermal-vacuum

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degassing of a material prior to service will provide a significant benefit only in the case where the outgassing is primarily desorption or diffusion.

It must also be recognized that multiple outgassing mechanisms may occur simultaneously. In certain cases multiple fractions may diffuse to the surface, each having its own kinetics, or a high rate diffusion process plus a slow rate decomposition process may occur concurrently. This may have obscured the interpretation of experimental data in earlier work and the use of the kinetics approach can resolve many of those problems once the constants are known.

The Micro-VCM test (ASTM E595-77) is currently employed for evaluating materials as possible sources of contamination on a spacecraft. This test is essentially a go/no-go test which measures the mass loss of a specimen in 24 hours under vacuum at a fixed temperature of 125°C, and the amount of the outgassed material which will condense on a surface at 25°C. However, this test will not provide any clues as to the amount of contamination that might occur with more typical spacecraft temperatures and for the extended durations spacecraft are required to be in service.

This technical note describes a method for providing such information by a thermokinetics approach. It will be shown that this approach is a very powerful tool for such estimations and, in addition, sheds light on the specific mechanisms involved.

2.0 OUTGASSING PARAMETRICS

2.1 Basic Reaction Kinetics

The outgassing of polymeric materials is accompanied by a weight loss of the source which can be described by reaction rate kinetics. The rate of weight loss, whether due to decomposition, desorption, diffusion or evaporation, is a function of the instantaneous reacting weight (w) and is:[1,2,3,4]

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1. Superscripts in text designate references at end of paper

$$\frac{dw}{dt} = -k\,w^n \tag{1}$$

The exponent n is the order of the reaction and k is a proportionality constant which is temperature dependent. This temperature dependence is assumed to follow the Arrhenious principle:

$$k = A\,e^{-E/RT} \tag{2}$$

where E is the activation energy, R is the gas constant and A is a proportionality constant which is independent of temperature.

Substituting Eq (2) in Eq (1) and integrating from initial conditions (w_0, t_0) to any subsequent time (w, t) the residual weight remaining may be expressed as:

for n = 1

$$w = w_0\,e^{-kt} \tag{3a}$$

$$w = w_0\,e^{-tA\,e^{-E/RT}} \tag{3b}$$

for n $\neq$ 1

$$w = \left[w_0^{1-n} - kt(1-n) \right]^{\frac{1}{1-n}} \tag{4a}$$

$$w = \left[w_0^{1-n} - (tA\,e^{-E/RT})(1-n) \right]^{\frac{1}{1-n}} \tag{4b}$$

However, for outgassing purposes, it is the weight loss that we are primarily interested in, or the fraction of the original weight that is lost. The latter is obviously ($1-w/w_0$), and we can rewrite Eqs (3) and (4) to give weight loss directly as a function of time, temperature and the thermokinetic constants as:

for n = 1

$$1 - \frac{w}{w_0} = 1 - e^{-kt} \tag{5a}$$

$$1 - \frac{w}{w_0} = 1 - e^{-tA\,e^{-E/RT}} \tag{5b}$$

for $n \neq 1$

$$1 - \frac{w}{w_o} = 1 - \left[1 - \frac{(1-n)kt}{w_o^{1-n}}\right]^{\frac{1}{1-n}} \qquad (6a)$$

$$1 - \frac{w}{w_o} = 1 - \left[1 - \frac{(1-n)t A e^{-E/RT}}{w_o^{1-n}}\right]^{\frac{1}{1-n}} \qquad (6b)$$

It is apparent from Eq (5) that the total quantity of outgassing products (as a fraction of the total material initially present) in a first-order reaction is a relatively simple exponential, and can be simply plotted or otherwise described. However, for reaction orders other than unity (Eq (6)), the fraction lost is a function of the finite amount present initially, as well as a function of time and thermochemical constants. In the case of zero-order reactions (n = 0) the rate of weight loss is invariant, and may be controlled by some other factor such as available surface area or rate of heat input. The evaporation of liquids are frequently zero-order as in the case of glycerine[5] or DC-704 silicone oil[6]. There is strong evidence that most outgassing is primarily first-order, but the possibility of nonunity orders cannot be ruled out pending more exact testing and analysis.

The value of the reaction constant A usually has a basis in the underlying reaction. In bimolecular reactions (second-order), the value of A may be interpreted as the number of molecules colliding.[7] However, in unimolecular reactions (first-order), the value of A is believed to be related to the frequency of oscillation of the atoms within the molecule, which is usually of the order of 10^{13} per sec. Deviations from this value however are not unusual. Data on the decomposition of TFE Teflon[8] for instance shows it to be a first order reaction with A = 4.73 x 10^{18} sec^{-1} and E = 80,500 cal/mole.

One of the assets of the thermokinetic approach is that the numerical value of the activation energy provides a clue to the specific mechanism involved in outgassing. The orders of magnitude of activation energies for polymers are:[9] 1-10 kcal/mole for desorption; 5-15 kcal/mole for diffusion and evaporation; and 20-80 kcal/mole for thermal decomposition. As discussed briefly in a later section, the values of the activation energy and specific reaction constant can be determined from TGA experiments.
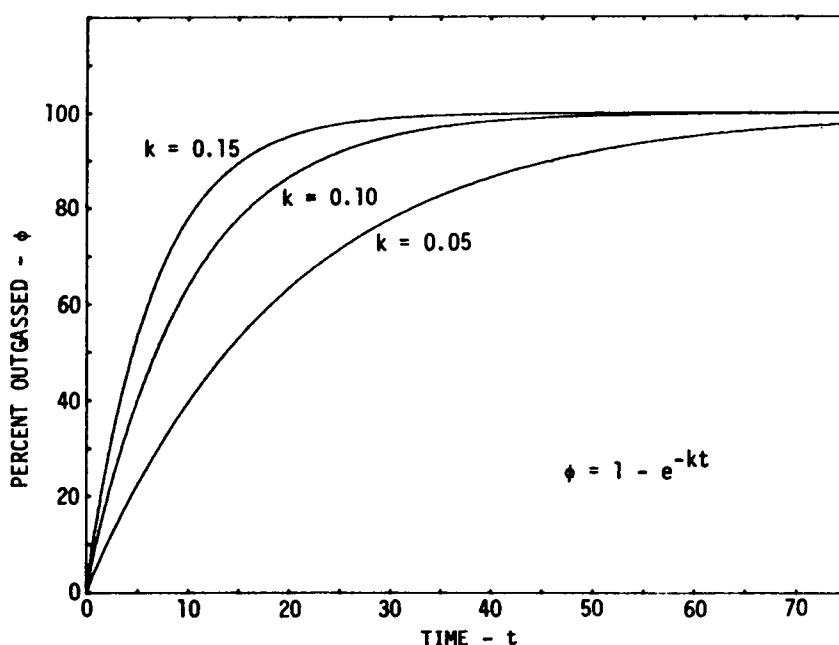

FIGURE 1 PREDICTED OUTGASSING ASSUMING A FIRST-ORDER REACTION

2.2 Comparison of Theory with Experimental Results

A plot of the total accretion of outgassed product with time is shown in Figure 1 for several reaction rate coefficients, assuming a first-order reaction (Eq 3a). This figure shows a high initial rate, and the rate decaying with time, with the total quantity outgassed becoming asymptotic to the total available amount of reactant.
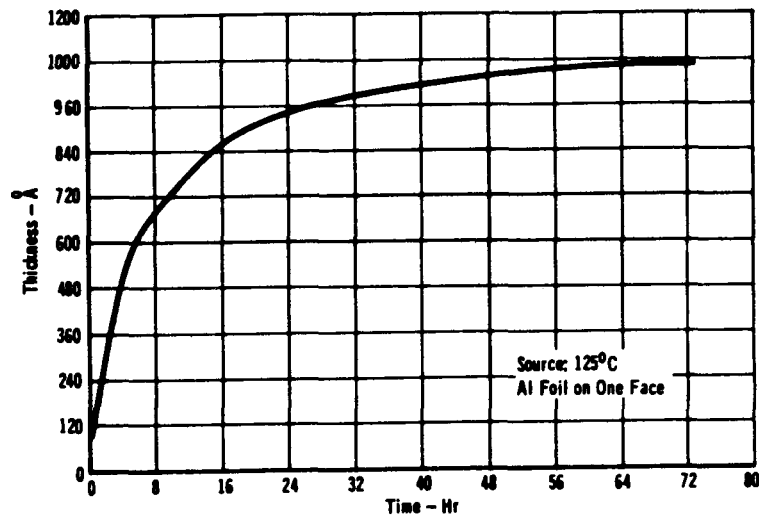
FIGURE 2   MEASURED OUTGASSING OF RTV-602 SILICONE AT 125°C

Experimental data for long term outgassing of RTV-602 under closely controlled conditions is shown in Figure 2. This data was obtained at MDAC-St. Louis using procedures previously described.[6,10] The close similarity of Figures 1 and 2 is obvious.

Theoretically it is possible to obtain data, such as shown in Figure 2, at a series of different temperatures in order to obtain the required constants. However, experimental difficulties have demonstrated that this is not practical. At low temperatures contamination rates are so low that the test becomes prohibitively long, and difficult to distinguish between chamber background and true contamination. At high temperatures, the heat-up time of the Knudsen cell allows the more volatile fractions to evaporate before the temperature stabilizes at the test temperature.

A considerable body of outgassing data exists, run under varying conditions and temperatures. Invariably the data have all the hallmarks dictated by Equation 3: rapid outgassing initially, an exponentially decaying rate, and the total quantity assuming a nearly

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asymptotic value. As an example, the data of[11] covered a number of different materials, measured at different temperatures by different techniques. Those data should conform (if first-order reactions) to a simplified version of Equation 3a where the fraction outgassed (ϕ) is:

$$\phi = 1 - e^{-kt} \qquad (7)$$

The empirical equations contained in[11] have been rearranged to this form and are shown in Table I. The values of k are expected to vary due to the differing materials and temperatures. The essential point here is whether the data conforms to the general $1 - e^{-kt}$. This correlation appears quite good.

Table I Outgassing of Silicones

Material	Source Temperature °C	Measurement Technique	Fraction Outgassed (t = Hours)
RTV-602	140	Knudsen Cell QCM	$1.002 - e^{-0.579t}$
Modified RTV–602	180	Knudsen Cell IR Ellipsometry	$1.02 - e^{-0.917t}$
RTV–560	140	Knudsen Cell Vis. Ellipsometry	$0.99 - e^{-0.383t}$
RTV–566	50	2.5"x2.5" Flat Plate QCM	$1.01 - e^{-0.539t}$

Curran and Millard in a recent paper[16] have presented data on the contamination of a satellite in a geosynchronous orbit. Their data is shown in Figure 3, and which, except for a translated zero-point, shows the characteristics expressed by Eq 3a.
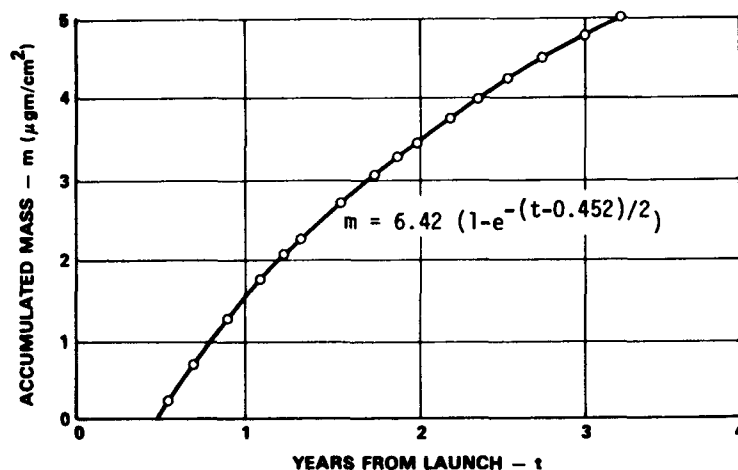
FIGURE 3   CONTAMINATION MEASURED ON A GEOSYNCHRONOUS SATELLITE
AFTER CURRAN AND MILLARD (REF 16)

2.3   Estimated Outgassing as a Function of Activation Energy

The first-order reaction equation (Eq 3b) can be manipulated to:

$$\ln(\ln w_0/w) = \ln t + \ln A - E/RT \tag{8}$$

which provides a convenient form for estimating the amount of outgas-
sing that will occur. Figures 4 and 5 show this data for 25°C and
125°C respectively. In both cases, the specific reaction constant,
A, was assumed* to be 1×10^{13} sec^{-1}. The maximum total weight loss
(TWL) permitted under NASA requirements (1% in 24 hrs at 398K) is also
shown for reference. While the scale of the ordinate on Figures 4 and 5
is $\ln (\ln w_0/w)$, the scale is marked in units of the equivalent frac-
tion (ϕ) of outgassed material with $w_0/w = 1/(1 - \phi)$. The separate

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*the correct unit for A is W^{1-n}/t; however for first-order reactions
assumed here, this becomes reciprocal time. It might be noted also that
the units of k, A and t can present a trap for the unwary. They must
be consistent.

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scale to the right on these two figures shown the effect of higher (10A) and lower (0.1A) multiples of the assumed A.

For comparison with the NASA limits of outgassing based on the Micro-VCM test, a linear plot of Equation 3b is shown in Figure 6.

It is apparent from these figures that if the activation energy is higher than about 36,300 cal/mole ($A = 10^{13} sec^{-1}$), that the material will pass the test even though ultimately all of the material will outgas. Also when the activation energy is substantially less than 36,000 cal/mole, in the diffusion range for instance (5-15 kcal/mole), that the outgassing will be very rapid and such a material will satisfy NASA requirements only if the total reactant is less than 1% of the
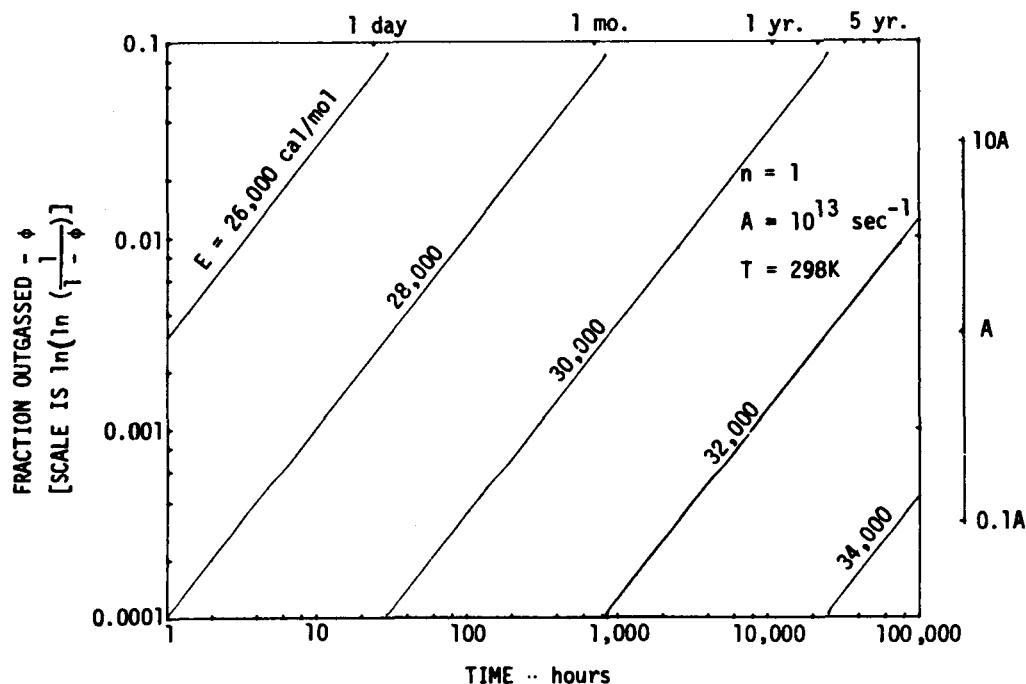
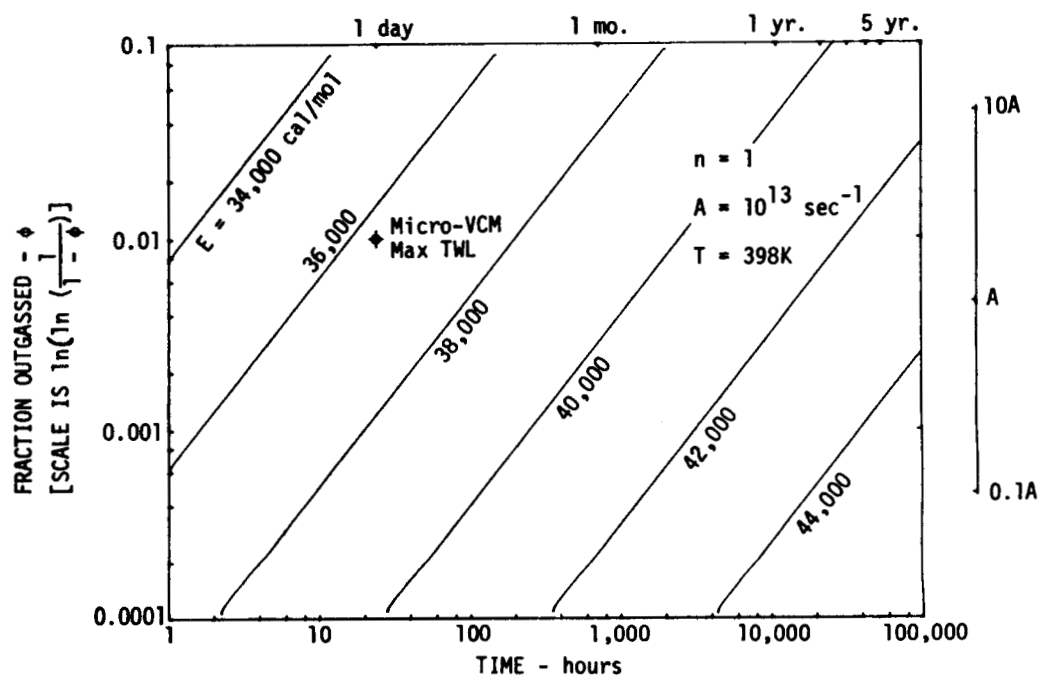

FIGURE 4 OUTGASSING AT 25°C, FIRST-ORDER REACTION

FIGURE 5 OUTGASSING AT 125°C, FIRST-ORDER REACTION

total mass of the host material. It should be pointed out that where the outgassing originates from unreacted catalyst or monomer, this is likely to vary from batch-to-batch. Fortunately, this situation appears to be the one most amenable to preservice thermal-vacuum treatment to reduce outgassing.

2.4 Effect of Temperature on Outgassing Rate

The effect of temperature on relative outgassing for a material may be derived by rewriting Eq 1:
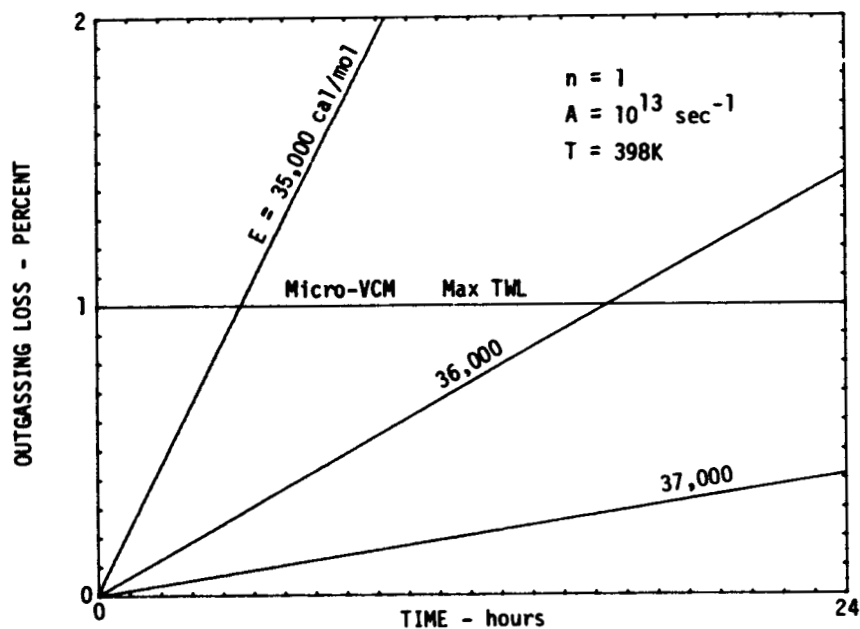
$$\frac{dw}{dt} = -A\,e^{-E/RT}\,w^n$$

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FIGURE 6 OUTGASSING AT 125°C, FIRST-ORDER REACTION

and

$$\frac{dw/w^n}{dt} = -A\,e^{-E/RT}$$

were dw/w^n is the fractional weight loss. By writing this equation for two temperatures and dividing, we have

$$\frac{\left[\dfrac{dw/w^n}{dt}\right]_{T_2}}{\left[\dfrac{dw/w^n}{dt}\right]_{T_1}} = e^{\frac{E}{R}\left\{\frac{1}{T_1}-\frac{1}{T_2}\right\}} \tag{9}$$

Thus we see that the relative rate of fractional weight change with temperature will vary for different activation energies. The effect of

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temperature on the outgassing rates relative to 125°C for various ener-
gies of activation is shown in Figure 7. It is seen that as the energy
level increases, the temperature effect is much higher. Scialdone[9]
obtained this identical result through a somewhat different approach.
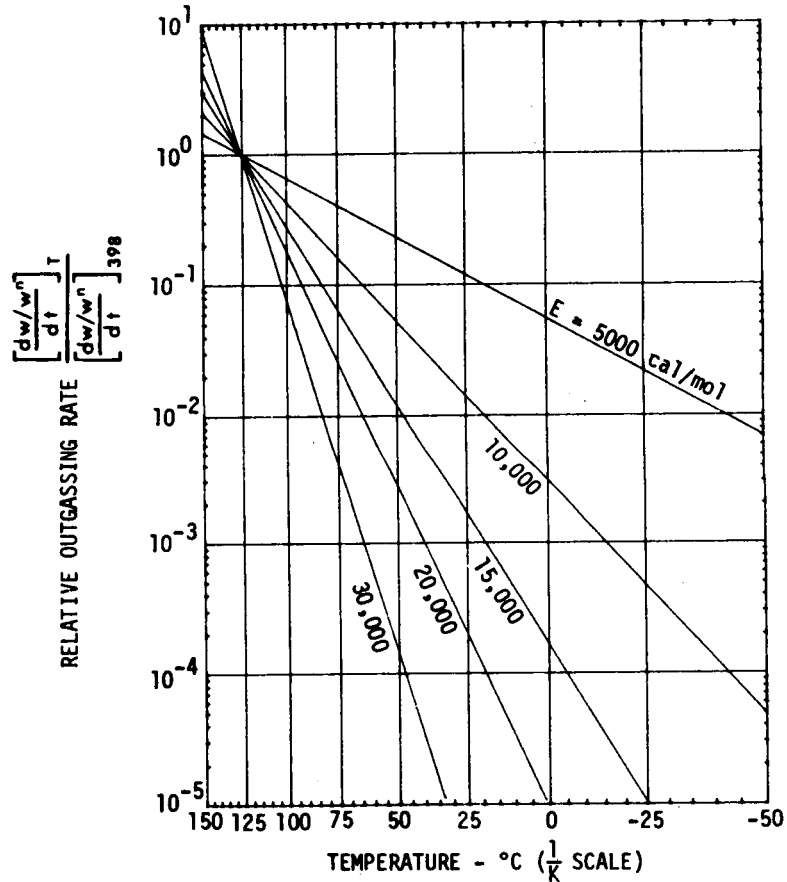

FIGURE 7   EFFECT OF TEMPERATURE ON OUTGASSING RATES
REFERENCED TO 125°C

2.4   Effect of Time on Outgassing Rate

Equation (1) described the outgassing rate as a function of active
mass available for outgassing. The integrated form of that equation
(Eq 3 and 4) described how the active mass changed with time. By
substituting Eq (3) and (4) into Eq (1) we find that the rate of change
of available mass (which is the outgassing rate) is:

for n = 1

$$\frac{dw}{dt} = -kw_0 e^{-kt} \qquad (10a)$$

for n ≠ 1

$$\frac{dw}{dt} = -k\left[w_0^{1-n} - kt(1-n)\right]^{\frac{n}{1-n}} \qquad (10b)$$

Equation (10a) shows that the outgassing rate for a first-order reaction would decay exponentially with time, the same result which has been determined empirically[6,10,11,12].

For a zero-order reaction, Eq (10b) shows that the outgassing rate is constant at all times, and which has been previously noted as occurring with simple liquids and monomers. For other than zero-order or first-order reactions, the rate will vary in a complex manner, which has been observed by several investigators[13,14,15]. It can be seen from Equation (10b) that the reaction rate for $0 \leq n < 1.0$ will decrease to zero in a finite time:

$$t = \frac{w_0^{1-n}}{(1-n)k} \qquad (11)$$

However, for reaction orders of 1.0 or larger the rate can never reach zero, though for practical purposes it may become insignificant after long time periods.

Figure 8 illustrates the typical shapes of outgassing rate curves for various reaction orders, with the assumption of equal rate constants. Figure 9 makes the same rate constant assumptions and shows how the total outgassed quantity varies with time for different reaction orders. The equal rate assumption is made for purposes of illustration only. With real materials they can be expected to vary widely.
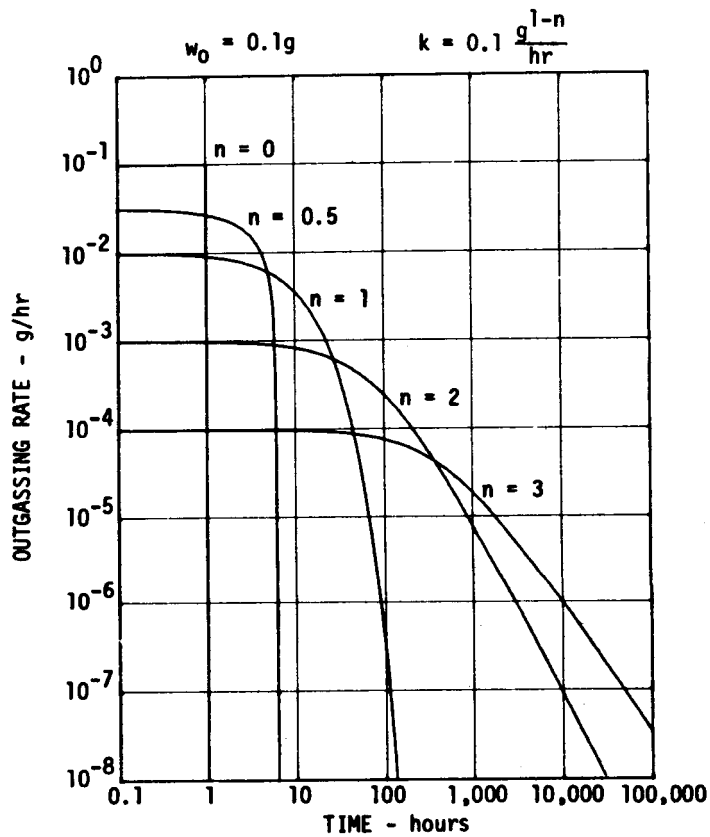
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FIGURE 8   EFFECT OF REACTION ORDER ON OUTGASSING RATES

3.0   DETERMINATION OF CONSTANTS

The determination of the constants for use in the kinetics approach to outgassing is a complex subject and will be only briefly reviewed here.

The constants can be determined by outgassing measurements made at a series of constant temperatures. However, there are a number of flaws in this approach:

- o Long test durations are needed to fully characterize the data (70-100 hours), even at high temperatures (125-200°C).
- o Loss of material (low energy of activation material) during heat-up to test temperature.
- o At low temperatures, measurement of the minute quantities are extremely difficult and subject to gross errors.

Because any test will likely be used not only for initial evaluation of material, but also for evaluating individual mixes of material used in production, it is desirable that a shorter test be available. In this respect even the Micro-VCM test requires a minimum of 3 days to run, when the pre- and post-test conditioning is included.
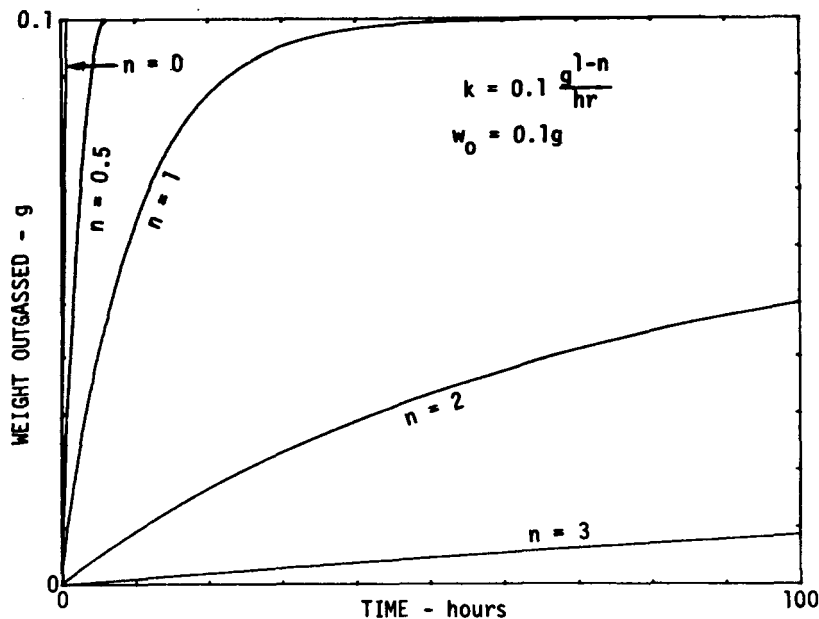

FIGURE 9 EFFECT OF REACTION ORDER ON TOTAL QUANTITY OUTGASSED WITH TIME

The approach that is likely to be most applicable is dynamic thermal gravimetric analysis. In this test, the specimen is exposed to a constant rate of temperature rise, usually beginning at room temperature. With a constant rate of temperature change:

$$\frac{dT}{dt} = \beta$$

$$dt = \frac{dT}{\beta}$$

so the basic equation:

$$dw = -A e^{-E/RT} w^n dt$$

can be expressed in terms of temperature:

$$\frac{dw}{w^n} = -\frac{A}{\beta} e^{-E/RT} dT \qquad (12)$$

By evaluating the weight change as a function of the temperature during a TGA, the kinetic constants may be determined. When consecutive or concurrent reactions are occurring with different constants (believed to be a frequent occurrence in outgassing), the data analysis becomes quite difficult, but not impossible. An obvious advantage of this type of test is that even with modest rates of temperature rise, the test need not take more than a few hours.

The critical constants required to be determined are the activation energy (E), the specific reaction constant (A), reaction order (n), and the mass of the reactant available. Because of the last requirement it is imperative that the TGA be carried to final constant weight, and that it be conducted in the atmosphere of operational service (vacuum).

4.0 CONCLUSIONS

Previous attempts to model the outgassing of materials have not been completely successful, due to a lack of understanding of the mechanisms and materials participating. However, the application of chemical reaction rate kinetics appears to offer a valid approach to resolving this problem. To implement this approach it will be necessary to have knowledge of various constants, which presumably can be obtained through thermalgravimetric analysis. With the constants available, this method will provide the systems engineer with a comprehensive model to predict outgassing as a function of both time and temperature. If the TGA data indicates an outgassing species is a minor constituent of the bulk material, the kinetics technique is capable of identifying a preservice vacuum outgassing procedure that should effectively eliminate that source. Under circumstances in which normally inert material is illuminated by intense electromagnetic energy, this technique should be capable of a reasonable estimate of outgassing that would occur under the temporary highly elevated temperatures.

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